Project no. 518307

ILHYPOS

Ionic Liquid-based Hybrid Power Supercapacitors

a “Specific Targeted Research Project” under the 6th Framework Programme of the European Commission

Priority: Sustainable Surface Transport

Publishable Final Activity Report

Period covered: from 1.12.2005 to 31.05.2009

Date of preparation: 30.04.2010

Start date of project: 1.12.2005

Duration: 42 months

Project Coordinator name: Mario Conte
Project Coordinator Organisation name: ENEA

Revision [Final]

Report No.:	Publishable Final Activity Report	
Title	Publishable Final Activity Report – 1.12.2005 – 31.05.2009	
Report Status:	Version 1	
Report Date:	30 April 2010	
Author(s):	Mario Conte	ENEA
Contributors:	All WP Leaders	

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1 Introduction and approach with respect to the state-of-the-art

Project Objectives

The ILHYPOS Project aims at developing green, safe, and high specific energy and power Hybrid SuperCapacitors (SC) for application as peak power smoothing device in fuel cell (PEM) powered electric vehicles and, as an additional second option, in delocalised small energy production plants based on PEM fuel cells.

The Hybrid SCs to be developed are based on the use of Ionic Liquids as electrolytes. Ionic liquids are excellent ionic conductors, virtually non volatile and thermally stable up to 300°C. Their electrochemical stability window easily exceeds 5 V. These properties make ionic liquids excellent candidates as electrolytes in supercapacitors. The ILHYPOS has challenging scientific and technological objectives potentially able to overcome present technology limitations.

The scientific objectives already identified are: (1) Synthesis and characterization of an Ionic Liquid (or a mixture of Ionic Liquids) having improved properties (overall ionic conductivity, electrochemical, chemical and thermal stabilities) at low temperatures (down to -20°C), while maintaining its superior performance at 60°C and above with respect to present ionic liquids; (2) Synthesis of Electronically Conducting Polymers (ECPs) optimised for the use as positive electrode in Ionic Liquid-based supercapacitors by electrochemical techniques; (3) Identification of high surface area carbons (e.g. activated and aerogel carbons) optimised for the use as negative electrode in Ionic Liquid-based supercapacitors; (4) Investigations of the electrochemical performance of current collectors in Ionic Liquids based supercapacitors. Surface treatments will be developed onto the Al current collectors used in these hybrid supercapacitors to decrease the series resistance of the cells.

Competitive technological objectives have been also defined and the most interesting ones summarised in Table 1.

Table 1. Comparison of the theoretical energy density (E) for a discharge range from V_{max} to 0.5 V_{max} and maximum power density at matched impedance (P) of commercial supercapacitors and the ILHYPOS supercapacitors.

Supercapacitor type	Electrolyte	E[a] Wh/kg	P[b] kW/kg	Drawbacks
Carbon//Carbon	ACN-based	5	6	Safety
	PC-based	3	1	Low power; Reduced performance at T>40°C
Hybrid Carbon//ECP (SCOPE Project)	PC-based	3.5	2	Reduced performance at T>40°C
ILHYPOS Hybrid Carbon//ECP	Ionic Liquid	≥15	7	

ACN: Acetonitrile, PC: Propylene Carbonate

[a] $E=0.75(0.5CV^2)/w$; [b] $P=V^2/(4wESR)$ with capacitance (C), equivalent series resistance (ESR) and total weight of the supercapacitor (w), all based on experimental data.

Challenges/Problems addressed

Commercially available supercapacitors based on organic electrolytes suffer of limitations associated with the operating temperature. Temperatures above 40°C, frequently encountered within fuel cell powered vehicles and stationary (CHP=Combined Heat and Power or other possible usage, such as UPS) systems, may cause the degradation of the commercial

supercapacitors in terms of performance and safety. The volatility of organic solvents such as acetonitrile increases sharply with temperature making the devices containing them unsafe at 50-60°C. Moreover, ILHYPOS Supercapacitors relieves from more polluting chemicals largely used in present SC (organic electrolytes substituted by "green" ionic liquids).

Project structure/Technical approach

The project structure logically streamlines and cross-links all the activities related to materials R&D, materials and cell component scale up preparation and design and prototype construction up to final application-specific testing in order to better integrate expertise, equipment and needed development time to each major effort to reach efficiently and timely the project objectives.

The project was organised in 4 phases and 8 Work Packages (WP), integrating competence, experiences and facilities of the 8 participating organizations, presented in Table 2.

Table 2. List of participants (organisation name and country).

Participant name	Participant short name	Country
Ente per le Nuove Tecnologie, L'Energia e Lo Sviluppo Economico Sostenibile	ENEA	IT
Università di Bologna	UNIBO	IT
Université Paul Sabatier	CIRIMAT	FR
Degussa (now Evonik-Degussa)	Evonik	DE
Conservatoire National des Arts et Métiers	CNAM	FR
Arcotronics Technologies	Arcotronics	IT
Micro-vett	Microvett	IT
Leclanché Lithium (formerly Bullith Batteries)	LLG	DE

During ***PHASE 1 (Electrode & Electrolyte Materials R&D)***, academic and basic research organizations work was concentrated on the optimisation of the electrode and electrolyte materials in order to significantly improve the overall technical performances of each single component with the respect to present State-of-the-Art. With ***PHASE 2 (Development and Production (D&P) of SC Materials)***, the focus was on the scale up processes for optimising the materials production. In ***PHASE 3 (Application Requirements and Full-scale Prototype Production)***, an application specific study was performed by two end users in collaboration with a research organization as hybrid vehicle configuration investigator, and, based on these studies, Hybrid SC components were designed and assembled in the final prototypes. In ***PHASE 4 (Application Testing)***, testing procedures were developed and used to experimentally verify the performance of the prototype with the respect to the project targets. Figure 1 shows the project breakdown structure with the description of phases, work packages, tasks and relationships among them.

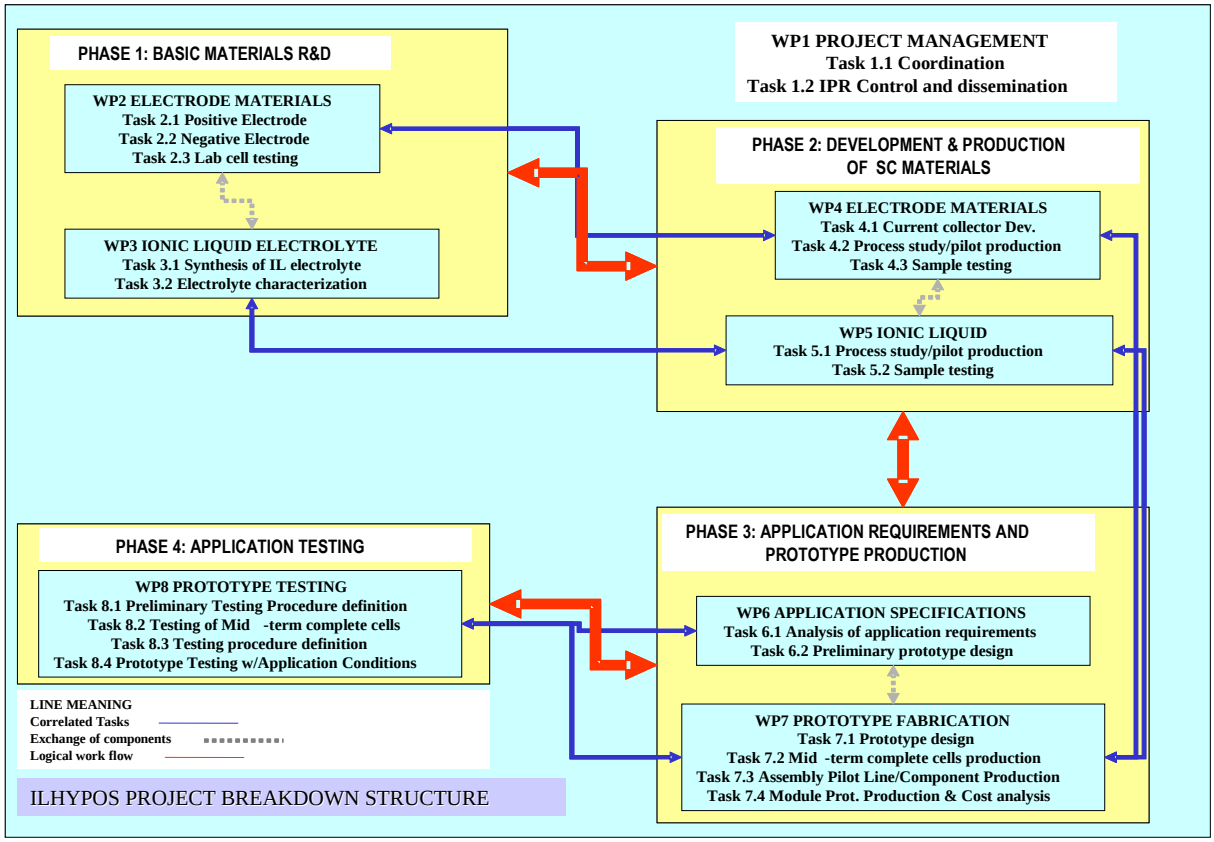

Figure 1. ILHYPOS Project Breakdown structure.

Detailed analysis of project objectives and comparison with state-of-the-art

The overall objectives of the ILHYPOS Project are of scientific and technological nature. Such objectives are summarised hereafter with S# (Scientific) and T# (Technological). Both objective types will have practical impacts on the final ILHYPOS SC:

S1. Synthesis and characterization of an Ionic Liquid (IL, or a mixture of Ionic Liquids) having properties (overall ionic conductivity, electrochemical, chemical and thermal stabilities) better than $PYR_{14}TFSI$ at low temperatures (down to -20°C), while maintaining its superior performance at 60°C and above;

S2. Synthesis of Electronically Conducting Polymers (ECPs) optimized for the use as positive electrode in Ionic Liquid-based supercapacitors by electrochemical techniques. Particular efforts will be devoted to the obtainment of polymer morphologies that would enhance the affinity of the ECPs for the ILs. The ECPs will also be characterized in full, lab-scale supercapacitors (coupled with high surface area carbon electrodes) to optimize the electrode material mass balance;

S3. Identification of high surface area carbons optimized for the use as negative electrode in Ionic Liquid-based supercapacitors. A large variety of high surface area are available for supercapacitor applications. Mesoporous carbons are the most often described (average pore size diameter between 2 and 50 nm) due to the use of the organic solvent that leads to a solvated ion size around 2 nm. Here, we will select optimized high surface area carbons, such as activated and aerogel carbons, compatible with the use of the Ionic Liquids in terms of pore size distribution, functional surface groups and density;

S4. Investigations of the electrochemical performance of current collectors in Ionic Liquids based supercapacitors. In supercapacitors, important contributions to the series resistance of the cell are the electrolyte resistance and the active material / current collector interface impedance. Surface treatments will be developed onto the Al current collectors used in these hybrid supercapacitors to decrease the series resistance of the cells.

T1. Prepare Ionic Liquids in large amounts, demonstrated at the 50/100 grams level and extended to the level of at least 2 kg per batch,

T2. prepare Electronically Conducting Polymer in large amounts, demonstrated at the 50/80 grams level and extended to the level of at least 2 kg per batch,

T3. prepare electrodes in large amounts, demonstrated at the level of 1-10 cm^2 and extended to the level of at least 1 m^2 per batch,

T4. develop the LAMCAP® technology (soft-packaged laminated capacitor), which should improve largely the performance of the hybrid super capacitor (specific energy and power), in order to make super capacitor modules of 2kF that weigh about 200 grams with the following estimated weight distribution:

- 38% composite electrode materials
- 25% electrolyte
- 18% current collectors
- 4% separator
- 15% case

The practical technical objectives at 60°C, resulting from the pursuing of the scientific and technological objectives are the following:

- display a maximum voltage (V_{max}) ≥ 3.5 V;
- reach a maximum specific energy of more than **15 Wh/kg** of stored energy;
- display an ESR < 5 mΩ in order to reach a maximum specific power (based on the maximum power transfer definition), of **7 kW/kg**, leading to practical power densities of more than **2 kW/kg** during 5 seconds according to the EUCAR procedure;
- reach the cycle life target of at least **100,000 cycles with 20%** maximum loss of capacitance, cycling between the maximum voltage and half of this same maximum voltage;
- reach a low cost of **25 Euro/kW**; and
- get a power loss lower than 50% by reducing the operating temperature from +60°C to +20°C.

In the entire project, S1 to S4 and most of from T1 to T4 (small and large batches) have been pursued: mainly research and development of materials (IL and positive and negative electrode materials, separators and current collectors), and related synthesis processes for major components in the SCs, and, more fundamental, their compatibility in an assembled cell. In addition, for T3 and T4, batches of produced materials have been used for developing SC fabrication processes, defining specification requirements for the selected mobile and stationary applications, and, finally, preparing and testing final prototypes of cells and modules. The scientific and technological achievements and drawbacks during the course of the project suggested some modifications and improvements to tackle minor performances of some components (reduced stability of ECP in ILs) by introducing three different cells designs and fabrication: symmetric carbon/carbon, Asymmetric carbon/carbon and, also, hybrid carbon/ECP (the only planned configuration), all using IL-based electrolyte.

Key components (such as ionic liquids and related processes, ECP) and commercial SCs have been continuously monitored by means of patent survey and literature/industry analysis. These analyses had a twofold scope: on one side to monitor the progress of the SC and adapt dynamically ILHYPOS work, on the other side to verify the possibility to develop novel materials, SC and preparation routes in competition with the existing ones.

Table 3 gives a direct comparison of the the project objectives and the final achievements, while Table 4 shows the specific performances (energy and power) of the project prototypes with respect to the intial targets.

Table 3. Comparison of ILHYPOS objectives and achievements.

Project Objectives	Achievements
S1	Selected and optimised IL with high ionic conductivity at 60 °C and at -20 °C
S2	Synthesised ECP cathode compatible with IL-based electrolytes
S3	Selected and optimised high surface area carbon for anode preparation (various kg)
S4	Identified specific current collectors compatible for SC uses with IL
T1	Prepared and fully characterized about 5 kg of IL (minimum 2kg)
T2	Produced in bulk production and fully characterized various compositions of ECP (various kg)
T3	Preparation of more than 100 m of electrodes for different SC design
T4	The LAMCAP® technology (soft-packaged laminated capacitor) has been substituted by the most advanced Wound Stack Technology and designed for SC cell preparation and assembly. More than 50 cells of different capacitance produced with a final assembly of 2 modules (5 cells each)

Table 4. Specific performance targets and achievements.

Cell design	Specific energy, Wh/kg	Specific power, kW/kg	Aim
Symmetric (Mid-term goals)	**24**	**5**	**Unplanned-Verify assembly process**
Hybrid	**51**	**13**	**Project targets**
Asymmetric	**40**	**13**	**New design unplanned**
Targets	**>32**	**10**	**Design level**

The most challenging performance characteristics of the ILHYPOS SCs are the high specific properties (energy and power) and working voltage, and the "green" nature of the components used in the ILHYPOS SC. The state of the art of a selection of commercial SCs is reported in Table 5.

Table 5. Summary of performance characteristics of commercial carbon/carbon SC cells [1]

Device or producer	Rated voltage V_R (V)	Capacit-ance (F)	ESR (mOhm)	Specific Energy (Wh/kg) (1)	Specific Power (W/kg) (95%) (2)	Specific Power (W/kg) Matched Load	Weight (kg)	Volume (L)
Maxwell*	2.7	2885	.375	4.2	994	8836	.55	.414
Maxwell	2.7	605	.90	2.35	1139	9597	.20	.211
ApowerCap**	2.7	55	4	5.5	5695	50625	.009	---
Apowercap**	2.7	450	1.4	5.89	2574	24595	.057	.045
Ness	2.7	1800	.55	3.6	975	8674	.38	.277
Ness	2.7	3640	.30	4.2	928	8010	.65	.514
Ness (cyl.)	2.7	3160	.4	4.4	982	8728	.522	.38
Asahi Glass (propylene carbonate)	2.7	1375	2.5	4.9	390	3471	.210 (estima-ted)	.151
Panasonic (propylene carbonate)	2.5	1200	1.0	2.3	514	4596	.34	.245
LS Cable	2.8	3200	.25	3.7	1400	12400	.63	.47
BatScap	2.7	2680	.20	4.2	2050	18225	.50	.572
Power Sys. (activated carbon, pro-pylene carbo-nate) **	2.7	1350	1.5	4.9	650	5785	.21	.151
Power Sys. (graphitic carbon, propylene carbonate) **	3.3 3.3	1800 1500	3.0 1.7	8.0 6.0	486 776	4320 6903	.21 .23	.15 .15
Fuji Heavy Industry-hybrid (AC/graphitic Carbon) **	3.8	1800	1.5	9.2	1025	10375	.232	.143
JSR Micro (AC/graphitic carbon)**	3.8	1000 2000	4 1.9	11.2 12.1	900 1038	7987 9223	.113 .206	.073 .132

(1) Energy density at 400 W/kg constant power, V_R - 1/2 V_R
(2) Power based on P_{MAX}=9/16(1-EF)*V^2/ESR, EF=efficiency of discharge*
** Except where noted, all the devices use acetonitrile as the electrolyte.*
*** all devices except those with ** are packaged in metal containers, these devices are in laminated pouches.*

Apart from the excellent values for the specific power in Table 5, which surely had a positive impact on ILHYPOS SCs working at higher voltages, the characteristics show that the ILHYPOS technical targets are still challenging and competitive with present products.

All the SCs in Table 5 are based on the use of acetonitrile (ACN) or propylene carbonate (PC) as electrolyte. These electrolyte materials have been abuse tested to verify the

[1] *A. Burke, M. Miller, Electrochemical Capacitors as Energy Storage in Hybrid-Electric Vehicles: Present Status and Future Prospects, Proc. 24th International Electric Vehicle Symposium EVS-24, Stavanger, 2009.*

level of hazards in case of leakage during operation at over voltage, over temperature and short circuit and sudden polarity reversal, showing limited hazard concern regarding the use of ACN in SCs, even if a limited production of HCN has been measured. Nevertheless, there is no evaluation of the environmental impact during fabrication and recycling or waste disposal of these electrolytes.

In addition, novel designs have been proposed as contingency plans to overcome some of the scientific and technological barriers encountered in the Project activities: the low stability of ECP in ionic liquid is strongly impacting the possibility to reach final performance targets, mostly in terms of cycle-ability; an asymmetric cell design still based on IL-based electrolyte, but using optimized activated carbon electrodes has been proposed and added to the original work plan with extra activities on specific materials, cell preparation and testing.

The update of the state-of-art confirms two fundamental pillars of the ILHYPOS Project: the Hybrid (or symmetric) Configuration with ionic liquid-based electrolyte may significantly increase the specific energy, because of the significant increase in working voltage, more than 3.5 V. Moreover, the use of ILs turns SCs into a “green” device in all the phases: production, usage and disposal.

2 Summary of chief results

In 3,5 years of the project, the activities have been, in-line with the planning, mainly devoted to the research and development of key materials for the preparation of SCs, together with the scale-up process analysis for the realization of SC components and the study of the application technical requirements. Finally, cell prototypes were produced and tested according to three (3) different designs confirming most of the project targets, with significant new inputs from novel asymmetric configuration and Wound Stack Technology for cell assembly. Open issues, still connected to scientific and technological challenges and developments, are related to the long term stability of various electrode materials in IL and the cost of the IL-based SC cells, which are still related to a limited production capability of IL precursors or components, not yet assisted by a real large-scale market.

Electrode materials R&D and scale up

UNIBO and CIRIMAT have been investigating and developing electrode materials and their compatibility with IL electrolyte. Furthermore, experimental activities have been carried out by CNAM for scaling up ECP production, and by Cirimat to select separators, proposed and supplied by Evonik, and to optimize current collectors.

Positive electrode materials

At UNIBO, ECPs have been produced via electrochemical processes and used for preparing composite electrodes, which have shown specific capacitance, close to the target value. For example, a clean galvanostatic polymerization procedure of pMeT [poly(3-methylthiophene)] has been developed, which preserves ILs from contamination of by-products derived from the cathodic reaction at the counter electrode. This procedure gives a pMeT electrode featuring 250 Fg^{-1} in ILs at 60°C, a very interesting result in view of application in IL-based hybrid SCs. Table 6 shows some ECS samples produced with electropolyme-

rizations and characterized with different electrochemical techniques (CV = Cycling Voltammetry and GLV = Galvanostatic Cycling).

Table 6. Specific capacity (Q_{pMeT}) and specific pseudocapacitance (C_{pMeT}) in ILs at 60°C as evaluated by the undoping CV curve at 20 mV s-1 with the maximum electrode potential V_{max} reached during the pMeT electropolymerization CV (EFc/Fc+ = EAg-0.2 V).

Polymerization conditions		pMeT mg cm^{-2}	pMeT performance in IL at 60°C			
IL	technique		IL	Q_{pMeT} mAh g^{-1}	C_{pMeT} F g^{-1}	V V vs Fc/Fc^{+}
$PYR_{14}Tf$	CV	3.4	$PYR_{14}Tf$	48	200	1.0
	GLV	4.7		61	210	1.1
	CV	3.4	$PYR_{14}TFSI$	48	175	0.8
	GLV	4.7		59	195	1.2
$PYR_{13}FSI$	CV	4.8	$PYR_{13}FSI$	61	255	0.9
	GLV	4.7		57	205	0.9
	CV	4.8	$PYR_{14}TFSI$	62	225	1.1
	GLV	4.7		60	180	1.2
	CV	5.6	$PYR_{1(2O1)}TFSI$ 20% $PYR_{13}FSI$ 80%	51	240	0.8
	GLV	4.0		66	270	0.7

Negative electrode materials

Analogously, many samples of the negative electrode have been prepared (by UNIBO) using different materials and purpose-developed cryo- and xero-gel carbons, and even starting from purchased activated carbons (CIRIMAT). Tests have been carried out to optimize the composition and the materials, when used with ILs, along with the experimental investigation of current collectors and specific separators.

In order to prepare carbonaceous carbon composite electrodes for supercapacitors the aero/cryo/xerogel carbon bars obtained by UNIBO after the pyrolysis step were milled to powders. Given that the *hard milling* did not significantly modify the porosity, UNIBO adopted such milling as standard procedure. However, some of the cryo/xerogel carbons which prepared by UNIBO resulted more brittle than the aerogel carbon, thus, *hard milling* dramatically reduced their mesopore surface and volume, also widening the pore-size distribution, and altered the intrinsic regularity of the cryo-xerogel carbon porosity. This was more evident when high dilution factors D were used as shown by the data for X6050B xerogel carbon prepared with D=60. Work at end allowed to select the best synthesis and milling conditions. In addition, activated carbon was heat treated to look for alternative anode materials.

CIRIMAT tested a lot of commercial activated carbons for anode materials and, then, assembled and tested symmetric cells with a new activated carbon coming from Arkema company. This carbon has a pore size in the high-microporous region, with more than 50% of the pore size between 1 and 2 nm (data from Arkema). According to a recent study CIRIMAT carried out, it was expected that this pore size distribution could lead to higher specific capacitance[2]. CIRIMAT started to study the performances of this activated carbon in $PYR_{14}TFSI$.

[2] "*Anomalous increase in carbon capacitance at pore size below 1 nm.*", J. Chmiola, G. Yushin, Y. Gogotsi*, C. Portet, P. Simon and P.L. Taberna, *Science*, **313**, 1760-1763 (2006)

CIRIMAT designed a special cell set-up to carry out the electrochemical characterizations of the CECA carbons, presented below (Figure 2).

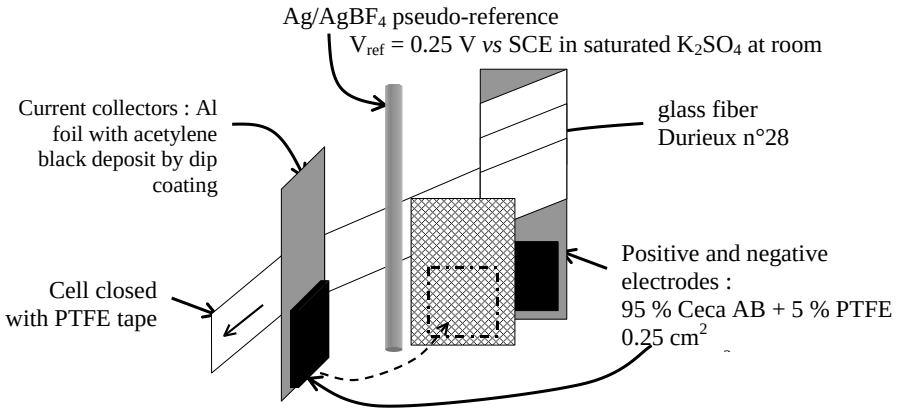

Figure 2. Cell configuration used for the voltammetry measurements at CIRIMAT.

The CECA AB negative electrode developed by CIRIMAT featured high capacitance in EMITFSI electrolyte (>100 F/g) to be improved in PYR-based electrolytes (70 F/g vs targeted value of 100 F/g), easy to process with PTFE binder (low content needed). Based on these results, CECA AB has been produced in large amounts (about 5 kg) and sent to Leclanche Lithium for electrode processing.

Positive electrode materials scale up

The work on hybrid supercapacitors is also progressed towards the scale up production of ECP for positive electrodes, carried out at CNAM. Grignard chemical reactors have been adapted for performing efficient electro syntheses of large amounts (100g/L) of electronically conducting polymers (e.g. poly methyl thiophene) in organic electrolytes (acetonitrile or propylene carbonate). The cell used was a Grignard reactor (Figure 3).

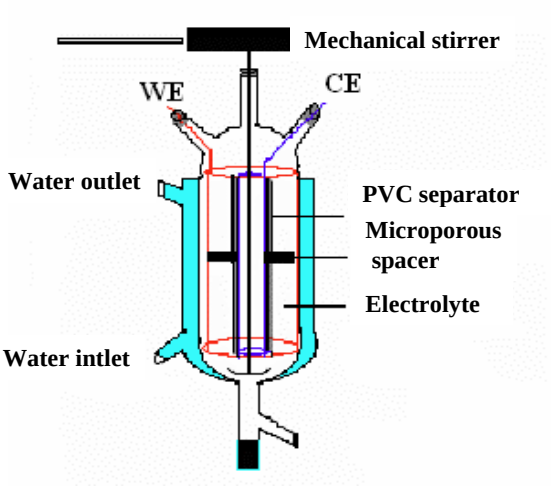

Figure 3. Grignard reactor used for the electro-synthesis of ECP (PolyMethylThiophene) powders.

The products can be washed and ground yielding materials in dry powdered form, stable at air, with granulometry in the micrometer range. In the last project period, a new, second, reactor of 3 L capacity was built, with electrodes made of plaques of platinized titanium for improving scalability and production. The best electrochemical properties (200 F/g

in PC) have been obtained by electro synthesis in propylene carbonate, but the yields are too low and the synthesis too expensive. The ECP products made at CNAM are able to be used for coating of aluminum collectors with appropriate binders and technology (work done at Leclanché Lithium). The capacitances of the electrodes are in the same range as the capacitances of activated carbon in ionic liquid (80-110 F/g), but not greater, as initially foreseen. At the end of the project a total amount of more than 3.5 kg of Pometil has been delivered to project participants for lab cells and prototypes preparations. In addition, a technology transfer work was started by CNAM with interesting results: electro synthesized conducting polymers in powdered form can be commercially obtained from a chemical company.

Separator and current collectors

Evonik has proposed the use of a proprietary separator, which is called Separion© (porous Alumina-based separator, 25 µm thick), mostly developed for lithium-ion batteries. Evonik, then, analyzed the use of its own separator, essentially made of porous ceramics, which has a unique feature in the market and might turn out to be of high importance due to the good wettability of the polar surface by ionic liquids. CIRIMAT tested this separator to verify its suitability for use at 60°C in ILs. The reference sample, for comparison, was a 300-µm thick glass fiber separator, which was already used for assembling laboraory cells. After various comparative tests on separators, it was decided to use the electrolyte vacuum impregnation process and the Separion© as separator, which allowed to save a significant part of the electrode volume thanks to the smaller thickness of the Separion (25 µm vs 300 µm). Finally, CIRIMAT has experimentally proved the cycling stability of several Al current collectors modified by the means of a surface treatment in the different electrolytes selected for the project. Neat (untreated) Al current collectors can be used to prepare electrodes for supercapacitors, but at the expense of a huge contact resistance between the active material film and the Al foil. A surface treatment onto Al foils, such as a conductive paint spraying, was able to greatly decrease this contact resistance.

Lab cell design and testing

The anode and cathode materials were used to build up laboratory cells for verifying stability and performances. On the basis of the experimental results on the negative and positive electrodes (based on 100% of ECP on current collector) the expected performances of hybrid supercapacitors with balanced electrode mass weights and operating at 60°C in defined ILs were well beyond the project target in terms of specific energy, based on the weight of active materials only: E_{max} of 55 Wh/kg with 3.9 V of maximum working voltage. The E_{max} target is also feasible with V_{max}=3.7 V (50 Wh/kg), much lower than the highest cell potential achievable with IL-based electrolyte, which can be considered a safe voltage for long cycling tests. The hybrid configuration (activated carbon/IL-electrolyte/ECP) showed some problems of stability in IL-electrolyte and alternative solutions were also pursued.

The optimization of recipes for electrodes and ILs has allowed the preparation of bulky amounts of raw electrode materials. The pMeT was produced by CNAM in batches via electrochemical synthesis. The samples (up to 250 g) were distributed after chemical and electrochemical characterization (best value of specific capacitance was 211 F/g with respect to the project target of 200 F/g) at various laboratories for testing and at LLG for developing the electrode production process. Furthermore, ILs scale up processes have been studied by Evonik, arriving to prepare the production of a few liters, after testing processes with limited yields.

During the execution of the project, CIRIMAT started the work by the full characterization of the selected carbon, which was considered as reference material that had to be sent to Leclanche Lithium for industrial negative electrode processing. CIRIMAT have then assembled several 2-electrode coin cells that have been tested in IL electrolyte. The coin cell sketch is presented in the Figure 4 below.

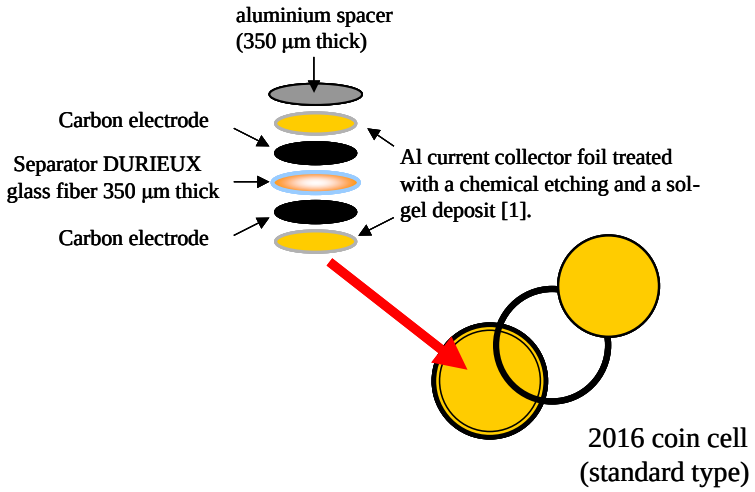

Figure 4. Coin cell used by CIRIMAT to assemble a symmetric carbon // carbon device.

The test results demonstrated the clear capability of cycling for the selected carbon at very high cell voltages (3.5V), meaning a low potential for the negative electrode in a hybrid system. The capacitance decrease with the cycling number was very low (10% after 40,000 cycles) and the capacitance change with the applied current is 50% when the current is increased from 10 to 100 mA/cm² (see Figure 5). Analogously, cell resistance was very stable during these 40,000 cycles at 60°C, always lower than 10 ohm.cm².

In summary, the tests proved the capability of cycling of the selected activated carbon with a capacitance of 75 F/g at 10 mA.cm² and a series resistance lower than 10 ohm.cm², stable during 40,000 cycles up to 3.5V. About 5 kg were produced and distributed for manufacturing negative electrodes for the project.

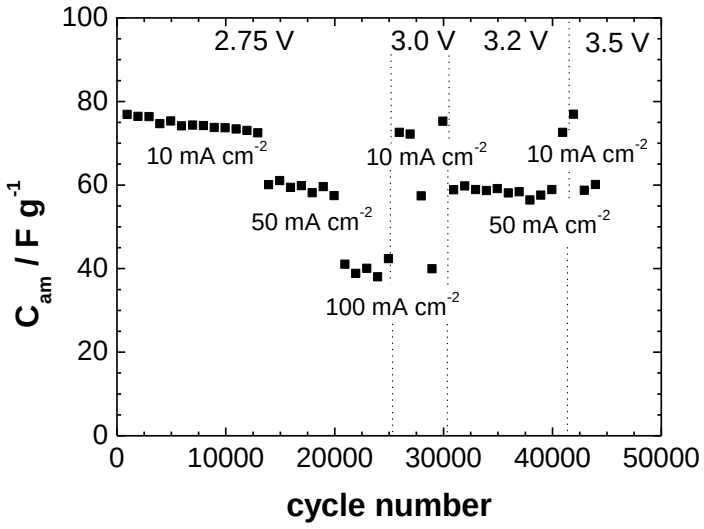

Figure 5. Capacitance vs cycling number of selected carbon material in IL electrolyte at 20 mV/s, in a 2-electrode coin cell 24x20; experiment, at 60°C.

Given that the performance of the hybrid supercapacitors with electrodes prepared with not optimized pMeT was uncertain to reach the ILHYPOS targets, asymmetric electrical double layer capacitors (AEDLCs) with the best performing carbon electrodes were in parallel designed, prepared and tested. These AEDLCs with carbon electrodes of different weight were able to reach a very high V_{max}, approaching more the high electrochemical stability window (ESW) of the ILs-based electrolyte, as shown in Figure 6, in which the working voltage of a symmetric carbon/carbon configuration is compared with that of an asymmetric one.

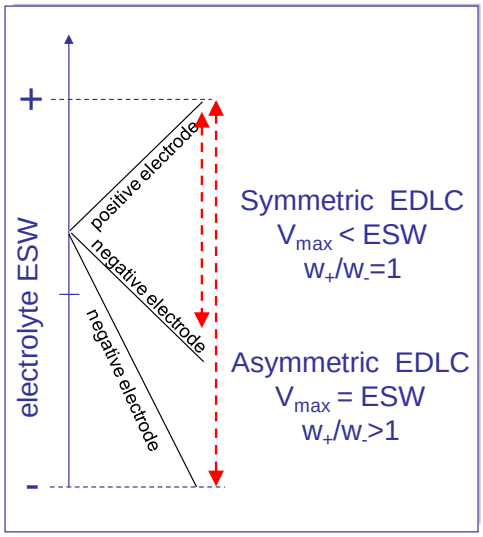

Figure 6. Asymmetric configuration advantages vs. symmetric configuration, with positive and negative double-layer carbon electrodes of different weight (w+, w-) to exploit the wide IL ESW.

Asymmetric EDLCs have been assembled with novel carbon electrodes, pre-industrially produced. Lab cells were used and tested with excellent performances (more than 25,000 cycles and specific energy and power in excess of 20 Wh/kg and 2 kW/kg), as can be seen in Figure 7.

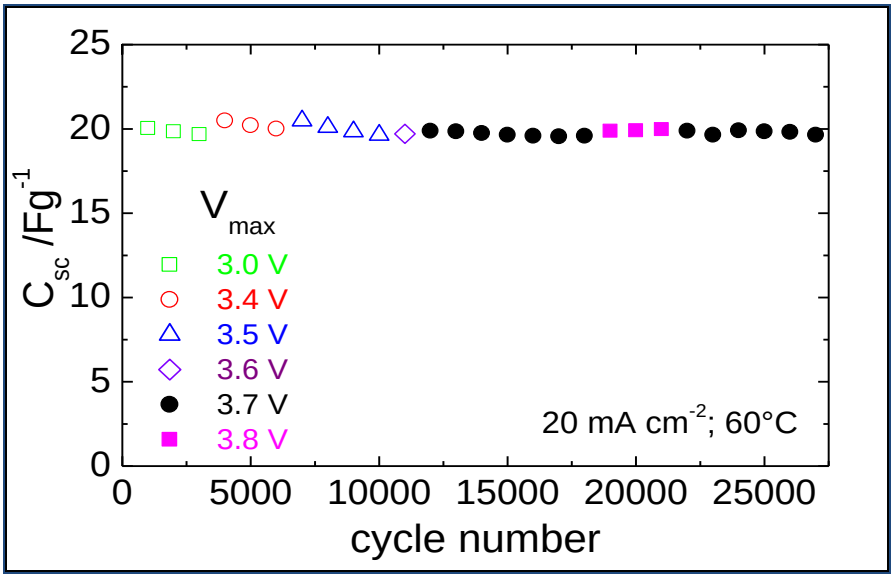

Figure 7. Typical galvanostatic cycles at 60°C PYR1(2O1)TFSI- AEDLCs deliver more than double energy than conventional EDLCs (with a fade of capacitance <5% on over 25,000 deep cycles with V_{max} of 3.5/3.8V).

The specific energy and power of AEDLCs are presented in a Ragone plot (Figure 8), where the behavior at different temperatures is also analyzed.

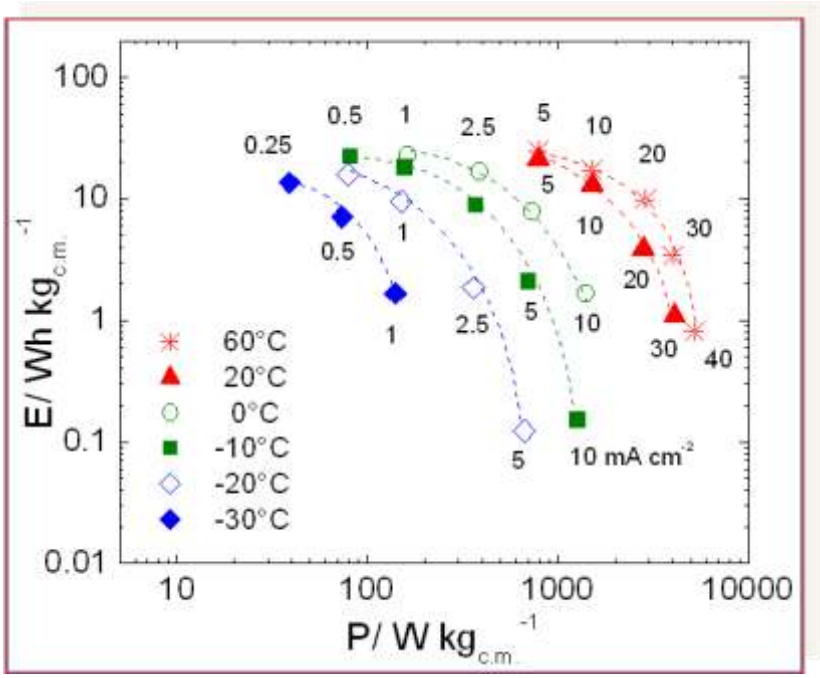

Figure 8. Ragone plot of ILHYPOS AEDLCs that operate in the wide temperature range for HEV applications.

The performance characteristics of AEDLCs were also compared to the targets of DOE-Freedom Car programme with promising results, as shown in Figure 9.

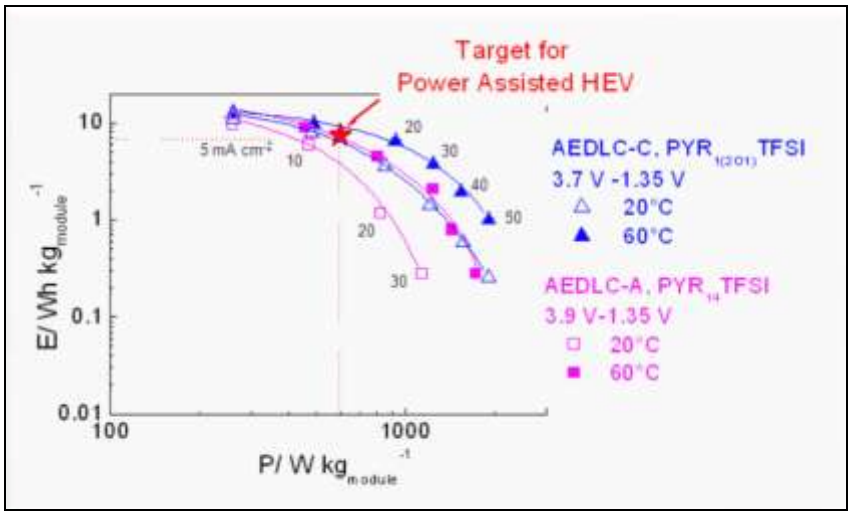

Figure 9. Performance of ILHYPOS AEDLCs with respect to DOE targets for power assist HEV.

Ionic-liquid based electrolyte R&D and scale up

In parallel to optimised electrode materials investigation, new ILs (and mixtures) have been synthesized using simple processes (one is an original aqueous route), fully characterized and then prepared in suitable quantities at laboratory scale (many batches up to 30g each) for verifying the compatibility (electrochemical stability up to 5V) and performance characteristics of electrodes materials with these new compounds. After selection

and characterizations at ENEA, scale up processes have been studied and optimized at Evonik up to the production of liter of IL for sample productions.

Ionic liquid R&D

Two new synthetic routes have been developed making use of ethyl acetate and/or water as the only solvent. The routes have been optimized in terms of chemicals weight and processing operative conditions. Both the routes allowed synthesizing extremely anhydrous, high purity materials with yields close to 90 mol%. The various ILs, synthesized in the ENEA Laboratory, have been characterized in various manners to verify thermal stability, ionic conductivity, viscosity and electrochemical stability window. Figure 10 shows the photo of an IL sample, which looks like water. In total, more than 40 different ILs were produced and investigated in a variety of compositions (see Table 7).

Figure 10. Photo of a $PYR_{14}TFSI$ IL sample synthesized by ENEA.

The chemical-physical properties of the synthesised IL may be summarized as the following:

i. all hydrophobic ILs have fully achieved the target of the project in terms of purity and water content;
ii. most of the ILs investigated showed a melting point below 20°C with a thermal stability up to 400°C both in nitrogen and air, thus achieving the project objective. Particularly, $PYR_{1(2O1)}TFSI$, $PYR_{1(2O2)}TFSI$ and the Im_{14}-based samples exhibited a melting point lower than -40°C;
iii. the viscosity resulted in good agreement with the conductivity data;
iv. most of the ILs exhibited an electrochemical stability window exceeding 5 V, thus matching the ILHYPOS target (Figure 11);
v. more than 10 ILs achieved the medium temperature ionic conductivity target (≥ 5 mScm-1 at 60°C) fixed in the project. On the contrary, no IL sample reached the low temperature conductivity target (≥ 1 $mScm^{-1}$ at -20°C).

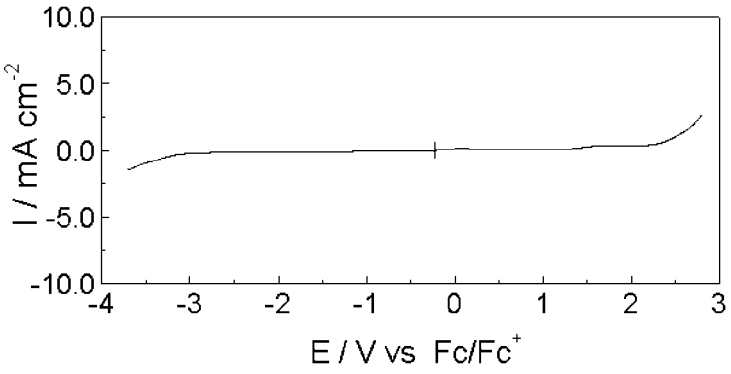

Figure 11. Electrochemical stability of $PYR_{14}TFSI$ IL.

However, the preliminary screening of IL mixtures seemed to be very promising since the mixtures showed a synergic combination of the properties (conductivity and melting point) of the starting ionic liquids. At the end of the project, the screening of the ionic conductivity of the IL mixtures allowed to identify the electrolyte mixture (0.2)$PYR_{1(2O1)}$TFSI-(0.8)PYR_{13}FSI (Figure 12) as matching the targets for IL. Therefore, this IL blend was further characterized in terms of thermal properties, viscosity and electrochemical stability. The comparison of achievements and targets on IL materials is summarized in Table 8.

Table 7. Hydrophobic ionic liquids synthesized at ENEA.

Ionic Liquid Name	Acronym
N-methyl-N-methylpyrrolidinium bis(trifluotromethanesulfonyl)imide	PYR_{11}TFSI
N-methyl-N-ethylpyrrolidinium bis(trifluotromethanesulfonyl)imide	PYR_{12}TFSI
N-methyl-N-propylpyrrolidinium bis(trifluotromethanesulfonyl)imide	PYR_{13}TFSI
N-methyl-N-*iso*-propylpyrrolidinium bis(trifluotromethanesulfonyl)imide	PYR_{1iso3}TFSI
N-butyl-N-methylpyrrolidinium bis(trifluotromethanesulfonyl)imide	PYR_{14}TFSI
N-isobutyl-N-methylpyrrolidinium bis(trifluotromethanesulfonyl)imide	PYR_{1iso4}TFSI
N-secbutyl-N-methylpyrrolidinium bis(trifluotromethanesulfonyl)imide	PYR_{1sec4}TFSI
N-methyl-N-pentylpyrrolidinium bis(trifluotromethanesulfonyl)imide	PYR_{15}TFSI
N-hexyl-N-methylpyrrolidinium bis(trifluotromethanesulfonyl)imide	PYR_{16}TFSI
N-heptyl-N-methylpyrrolidinium bis(trifluotromethanesulfonyl)imide	PYR_{17}TFSI
N-methyl-N-octylpyrrolidinium bis(trifluotromethanesulfonyl)imide	PYR_{18}TFSI
N-decyl-N-methylpyrrolidinium bis(trifluotromethanesulfonyl)imide	PYR_{110}TFSI
N-methoxyethyl-N-methylpyrrolidinium bis(trifluotromethanesulfonyl)imide	$PYR_{1(2O1)}$TFSI
N-ethoxyethyl-N-methylpyrrolidinium bis(trifluotromethanesulfonyl)imide	$PYR_{1(2O2)}$TFSI
N,N-dimethylpiperidinium bis(trifluotromethanesulfonyl)imide	PIP_{11}TFSI
N-ethyl-N-methylpropylpiperidinium bis(trifluotromethanesulfonyl)imide	PIP_{12}TFSI
N-methyl-N-propylpiperidinium bis(trifluotromethanesulfonyl)imide	PIP_{13}TFSI
N-butyl-N-methylpiperidinium bis(trifluotromethanesulfonyl)imide	PIP_{14}TFSI
N-methyl-N-pentylpiperidinium bis(trifluotromethanesulfonyl)imide	PIP_{15}TFSI
N-hexyl-N-methylpiperidinium bis(trifluotromethanesulfonyl)imide	PIP_{16}TFSI
N-heptyl-N-methylpiperidinium bis(trifluotromethanesulfonyl)imide	PIP_{17}TFSI
N-methyl-N-octylpiperidinium bis(trifluotromethanesulfonyl)imide	PIP_{18}TFSI
N-ethyl-N-propylpiperidinium bis(trifluotromethanesulfonyl)imide	PIP_{23}TFSI
N-butyl-N-ethylpiperidinium bis(trifluotromethanesulfonyl)imide	PIP_{24}TFSI
N-ethyl-N-pentylpiperidinium bis(trifluotromethanesulfonyl)imide	PIP_{25}TFSI
1-ethyl-3-methylimidazolium bis(trifluotromethanesulfonyl)imide	EMITFSI
tetraethylammonium bis(trifluotromethanesulfonyl)imide	Et_4NTFSI
tetrabutylammonium bis(trifluotromethanesulfonyl)imide	Bu_4NTFSI
N,N-dimethylpyrrolidinium bis(perfluotroethanesulfonyl)imide	PYR_{11}BETI
N-methyl-N-propylpyrrolidinium bis(perfluotroethanesulfonyl)imide	PYR_{13}BETI
N-butyl-N-methylpyrrolidinium bis(perfluotromethanesulfonyl)imide	PYR_{14}BETI
1-ethyl-3-methylimidazolium bis(perfluotroethanesulfonyl)imide	EMIBETI
tetraethylammonium bis(perfluotroethanesulfonyl)imide	Et_4NBETI
Tetrabutylammonium bis(perfluotroethanesulfonyl)imide	Bu_4NBETI
N,N-dimethylpyrrolidinium (perfluorobutanesulfonyl)(trifluotromethanesulfonyl)imide	$PYR_{11}Im_{14}$
N-methyl-N-*iso*-propylpyrrolidinium (perfluorobutanesulfonyl)(trifluotromethanesulfonyl)imide	$PYR_{13}Im_{14}$
N-butyl-N-methylpyrrolidinium (perfluorobutanesulfonyl)(trifluotromethanesulfonyl)imide	$PYR_{14}Im_{14}$
1-ethyl-3-methylimidazolium (perfluorobutanesulfonyl)(trifluotromethanesulfonyl)imide	$EMIIm_{14}$
tetraethylammonium (perfluorobutanesulfonyl)(trifluotromethanesulfonyl)imide	Et_4NIm_{14}
Tetrabutylammonium (perfluorobutanesulfonyl)(trifluotromethanesulfonyl)imide	BuN_4Im_{14}
N-methoxyethyl-N-methylpyrrolidinium trifluoromethanesulfonate (hydrophilic)	$PYR_{1(2O1)}$Triflate

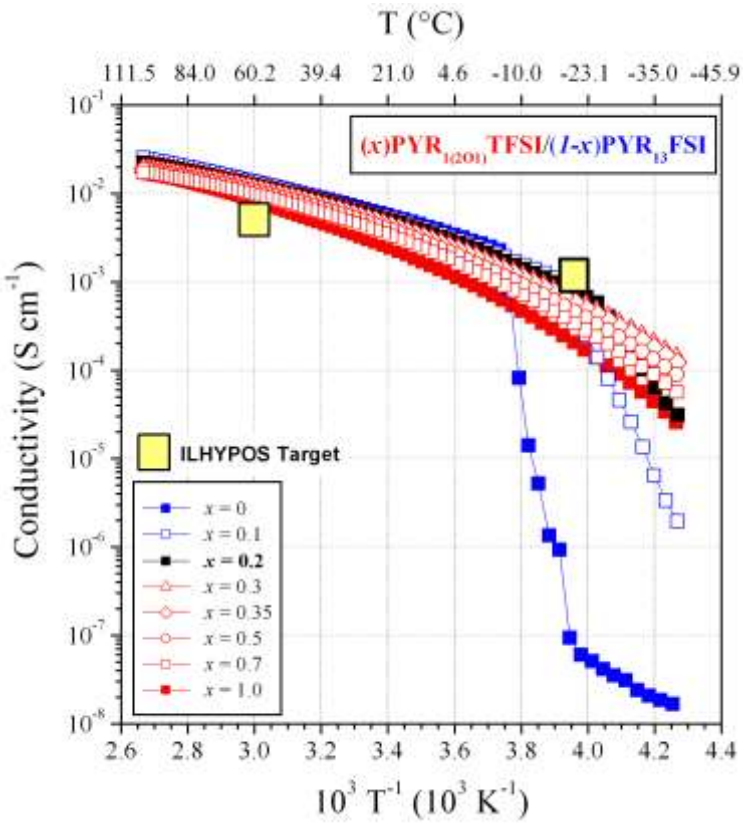

Figure 12. Conductivity vs. temperature dependence (x)PYR1(2O1)TFSI–(1-x)PYR13FSI IL mixtures.

Table 8. Comparison of achieved and planned targets for ILHYPOS ILs.

Properties of the mixture	*IL targets*	Results obtained from characterization
Purity	*> 99.8 wt.%*	> 99.5 wt.%
Water content	*< 20 ppm*	< 1 ppm
Conductivity at -20°C	*≥ 1 mS/cm*	0.8 m/Scm
Conductivity at 60°C	*≥ 5 mS/cm*	12.5 mS/cm
Thermal stability in air	*200°C*	210°C
Thermal stability in nitrogen	*250°C*	300°C
ESW (-20°C/90°C)	*≥ 5 Volt*	≥ 5 Volt (up to 60°C)

Ionic liquid scale up

The best ILs were selected and investigated by Evonik in terms of compatibility with a cost-effective bulk production process. All the samples produced were jointly characterized by Evonik and ENEA, until a final batch of IL has been prepared to produce the final SC prototypes by Arcotronics and Leclanchè Lithium. In total more than 3.5 kg of ILs have been produced, integrated by a complete set of tests covering, among others, viscosity, purity, and electrochemical stability window.

Application requirements

The ILHYPOS project addressed to key applications for SCs, both in conjunction with fuel cells (FCs): the use in hybrid electric vehicles (HEVs) with or without batteries; and the stationary application in uninterruptible power systems (UPS), which was selected during the

project, as more commercially interesting with respect to the initial combined heating and power (CHP) productions. For both applications, a preliminary analysis, supported by experimental data and simulations, was carried out by Arcotronics in collaborations with ENEA and Micro-vett to identify the technical requirements and the potential advantages achievable with the introduction of SCs. In order to establish the guidelines for the ILHYPOS SCs, the research team has investigated:

- SCs sizing both for HEV and FC-UPS
- The application of Supercapacitor for HEV –and FC-UPS
- The modelling and simulation of energy storage systems for HEV and FC-UPS.

Requirements for HEVs with fuel cells

A first definition of the SC size was carried out using the simulation results coming from the contribution of Micro-Vett and ENEA

In particular, Micro-Vett prepared a simulation of the electric vehicles based on a cost down model, while ENEA made a simulation starting from various general drive-train configurations to establish the possible role of SCs, by using the experience of ENEA on the dimensioning and management of hybrid drive train with electrochemical batteries, Fuel Cell and SCs. The general approach has been specialized for the reference vehicle selected in ILHYPOS (NEO FC van) to determine preliminary SC sizing.

The NEO (**N**o **E**mission **O**utfit) is a series-hybrid electric vehicle of the 'range extender' type, with a storage battery able to supply the traction power, while a FC system is able to recharge the battery and extend the vehicle range, well beyond that available with the battery alone (see Figure 13). The FC system power is lower than that required for moving the vehicle. The body of the NEO is that of an IVECO Daily van, powered by an Ansaldo electric powertrain with 30-kW continuous power and a 60-kW peak power (for 2 minutes). The rated powertrain voltage is 280 V, corresponding to the voltage of the 64Ah Zebra (Na-$NiCl_2$) battery system, see also Figure 14.

Figure 13. Micro-vett NEO FC reference vehicle.

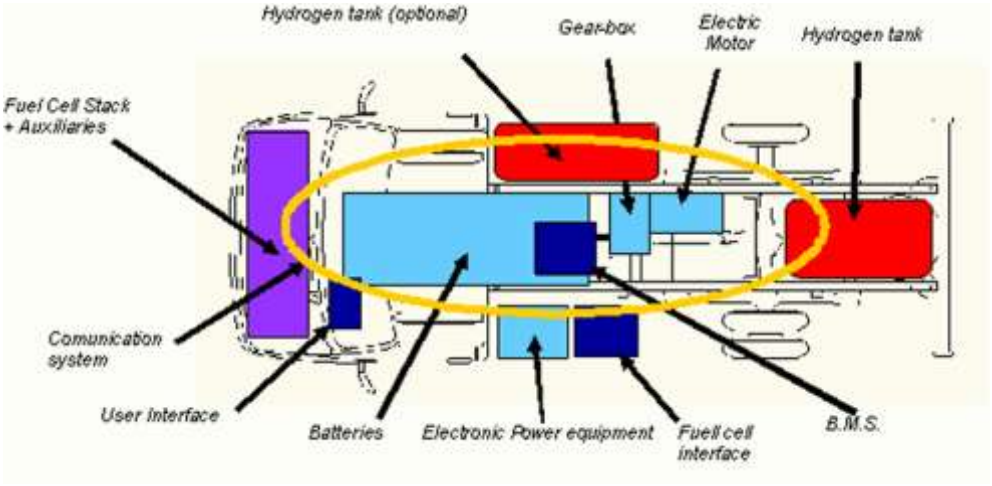

Figure 14. NEO FC vehicle layout.

Micro-Vett prepared a simulation (mainly based on a spreadsheet with formulas) of the FC electric vehicle based on an internal cost-down model. The software was made by Micro-Vett and is flexible enough to be used to simulate a city car or a medium weight truck. The software can show power requirements and also simulate a discharge on a standard cycle, such as ECE15, both urban and extra-urban phases.

The first part of the program describes the vehicle in terms of external dimensions, weight, wheel and transmission details. Then it focuses on the drive-train characteristics describing the motor and power device in terms of output torque, current and efficiency. This description is not a simple description of the overall characteristics of the drive-train, but considers also the real output torque of the motor. Basically, the vehicle is tested on a standard urban cycle, as described in ECE15 regulation, with peak speeds respectively of 15, 32 and 50 km/h. It is also possible to choose to run the extra urban part defined in the same regulation. The results of the simulation are presented in Figure 15.

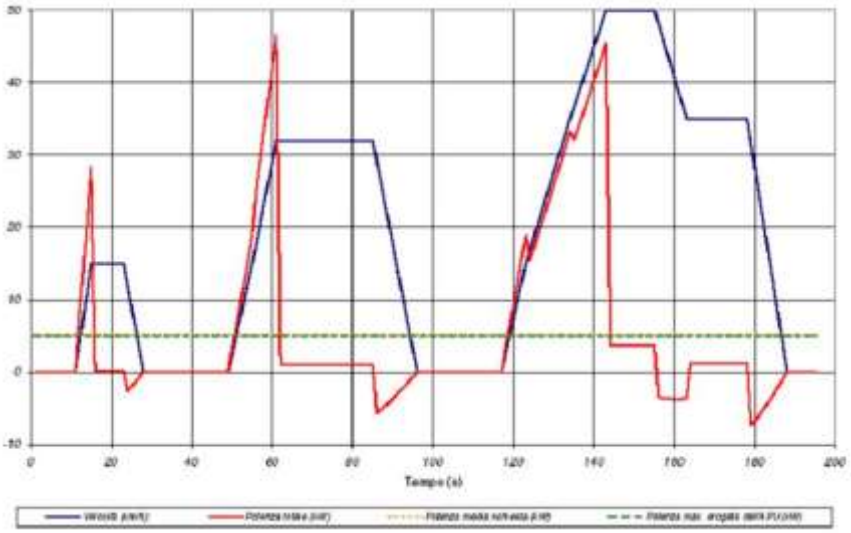

Figure 15. Simulation results for the NEO.

The work of ENEA has been concentrated on the modification of the drive-train configuration of NEO to consider the addition of the SC systems in order to reduce maximum current and peak power and extend cycle life. The analysis has been carried out with simula-

tion tools already developed and adapted to the modified NEO with SCs. The simulation tools consider energy management strategies and driveline configurations with simplifying hypotheses.

As a result of the simulation work, a general rule has been extrapolated by defining a numerical approximation index (*Fdr = Relative Dimensioning Factor*) aimed at quantifying the potential advantages in using SCs based on ILs in comparison with the conventional ones. The ratio *Fdr* is an indicative index (neglecting voltage drops and approximation in using integer numbers for series and parallel branches) for comparing SCs of different technologies, as demonstrated in Table 9.

Table 9. Fdr values for different SC comparisons.

SC types	Real	Approximated
Maxwell/Ness	1.66	1.69
Maxwell/ILHYPOS	1.61	1.68
Ness/ ILHYPOS	0.97	0.99

In particular, the comparison with commercial SCs from Maxwell and Ness is also interesting, by supposing the same energy content and a maximum working voltage for the ILHYPOS SC of 3.5 V (very conservative with respect to the potential). Table 10 summarises the results of such a comparison.

Table 10. SC dimensioning comparison.

Model	C (F)	V_{max} (V)	N_{cell}	SC weight (kg)
Maxwell	3000	2.7	93	256
Ness	5085	2.7	93	248
ILHYPOS	3000	3.5	72	95

The energy in Wh is calculated with the simulations along with the SC capacitance (C) and weight (without ancillaries: control device, case, thermal management and so on) and summarized in Table 11.

Table 11. ILHYPOS SC sizing.

C (F)	P_{max} (kW)	EC (Wh)	SC weight (kg)
24	33	176	11.8
36	33	276	18.4
29	41	217	14.5
44	41	331	22

Table 12 summarizes the results of the simulation with real values and in configurations with or without regenerative braking (RB). An estimation of the energy saving achieved with the use of SC is also reported in the last column.

Table 12. Potential energy saving with or without regenerative braking.

Cycle	Time [s]	Travelled distance [km]	Average speed [km/h]	Consumption (without RB) [H_2 g]	Consumption (with RB) [H_2 g]	Energy saving [%]
Ece urban	3510	18.3	18.7	650	440	32.3
Ece Micro-vett*	6557	42.8	23.5	736	701	4.0
Hyzem	3204	44	49.7	1504	1299	13.6
Hyzem_70	3204	32	38.5	970	780	19.6

** Speed and range not measured (supplied by Micro-Vett), mass 3.5 t with respect to 7.5 of the other simulations, RB (regenerative braking) limited.*

Requirements for FC-UPS

A similar analysis has been carried out for the use of SC in FC-UPS (uninterruptible power system with fuel cells). A real UPS station, from the Arcotronics factory of Vergato, was considered with a complete load diagram to support simulations (see Figure 16).

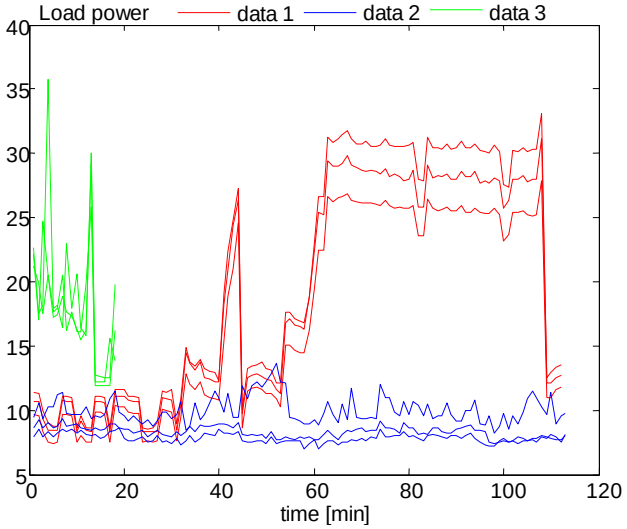

Figure 16. Vergato factory electrical load diagram.

Main results for a real case are reported in Table 13.

Table 13. ILHYPOS sizing for the FC-UPS simulation.

Model	Capacitance [F]	Vmax [V]	ESR [mΩ]	Cell Weight [kg]	N parallel	N series	Total weight [kg]
ILHYPOS	1700	3.5	2.29	0.19	1	71	13.5

Pilot process design and prototype fabrication

The preparation processes for the electrodes and for the cell assembly were developed by Arcotronics and Leclanché Lithium.

Electrode preparation processes

Leclanché Lithium developed new process for the preparation of PTFE-bound electrodes, based on activated carbons. They can be used both as supercapacitor electrodes and

as battery electrodes. Furthermore, a new process was developed for the handling and processing of electrically conducting polymers. The ECP prepared by the partner CNAM was a milestone. These polymers behaved in the coating process in a completely other way than the carbons. But also processes for milling, dispersing and coating of these polymers have been developed and tested.

A dry fibrillation process with PTFE as binder had to be developed. In this process the chemicals are mixed dry in an “Eyrich-Mixer”, then calendered to a belt and finally calendered to the collector grid with a second pair of sleeves. Figure 17 depicts the complete process.

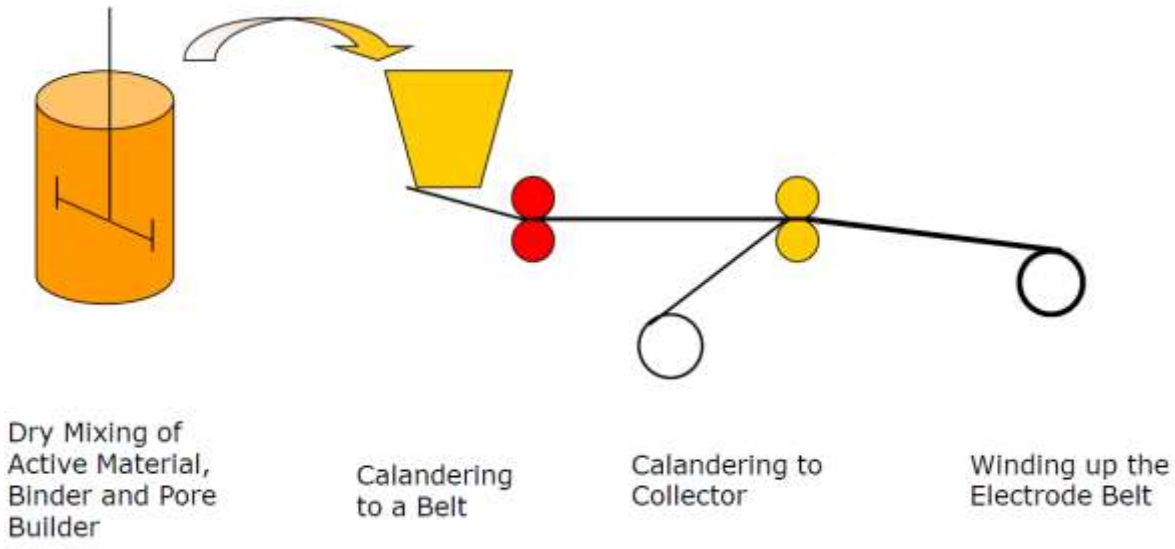

Figure 17. Schematics of the dry preparation process.

Finally coils of electrodes have been produced with the material supplied by the partners. The required collectors of Aluminium grids could be handled in the automated process.

Leclanché has learned in this project how to fabricate carbon-based and conducting-polymer-based electrodes with high performance. Pilot scale fabrication of electrodes has been carried out with various recipes, together with a preliminary cell design and pilot assembly line study. Expanded metals are foreseen to be used as collectors. A good electrical and mechanical contact is ensured by a thin intermediate layer. Therefore conducting paints have been applied to the metal in a pilot coater. Several molding methods have been tested. A total of 6 R&D loops have been necessary for producing samples of both electrodes. For the Positive Electrode, Leclanchè produced transferable coatings onto the backing film and transferred these coatings on the expanded metal.

The reels of the laminated films for both positive and negative electrodes were prepared (Figures 18, 19, 20 and 21). The electrodes have been supplied in several sheets.

Figure 18. Coating of electrode in industrial equipment.

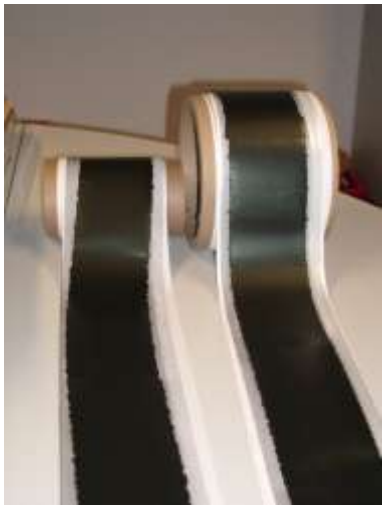

Figure 19. Coils of positive electrode.

Figure 20. Assembling electrode materials and collector.

The results showed a successful scale up with view to the laboratory recipes the partners gave to Leclanché Lithium. The task of the scale up from electrodes in the shape of coins to belts, produced in industrial surroundings was successfully solved with the final production and supply of more than 90 m of complete electrodes, double-sided, for both

asymmetric and hybrid configurations. Many samples were distributed to the various participants for laboratory testing.

Figure 21. Coil of the final electrode processed on Al-expanded metal collector.

Pilot cell design and assembly process

Arcotronics has carried out the cell design and pilot production line development for the assembly of the final cells and modules with the following steps:

- Pilot assembly line development and fabrication
- Final production of SC, with a target of 50 SC
- Module design and preparation
- SC Cost analysis

A complete pilot production line based on the results of the preliminary cell production and the latest technology used in the Li-ion cells assembly have been designed, fabricated and installed into the Arcotronics dry room. This pilot production line has been used for the preparation of the final production of SCs cells.

Arcotronics also analysed alternative processes in order to optimise the cell assembly methodology and the production cost of the SCs, starting from the initially proposed LAM-CAP® technology (soft package laminated capacitor), subsequently changed in a more innovative Wound Stack Technology.

A cost analysis of the developed SCs has been also performed, starting from the experience gained in the Li-ion industry. However, it was clear that the main issue in order to meet the project target is the IL-based electrolyte cost that is still far from the economic target of about one order of magnitude, even if, on the other side, a considerable cost reduction should be expected when volume production will increase.

The cell assembly is based on the ***Wound Stack concept***. In order to prove this concept, Arcotronics designed and fabricated manual pilot equipment (all the instrumentation for electrode cutting, tab welding, cell assembly, softpack insertion, electrolyte filling) capable of giving the complete cells.

Arcotronics cut many electrodes made with aluminum mesh and carbon coated (single and double-coated in the final design). Figure 22 gives an example of a complete electrode with welded tab.

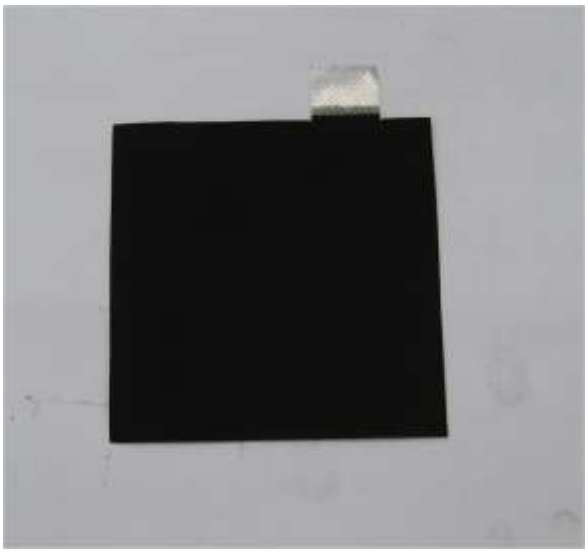

Figure 22. Coils of positive electrode.

Figure 23 describes the pilot production line process where complete SC ILHYPOS cells could be assembled, based on the wound stack approach, before putting into the bag, injecting electrolyte and sealing the final cell.

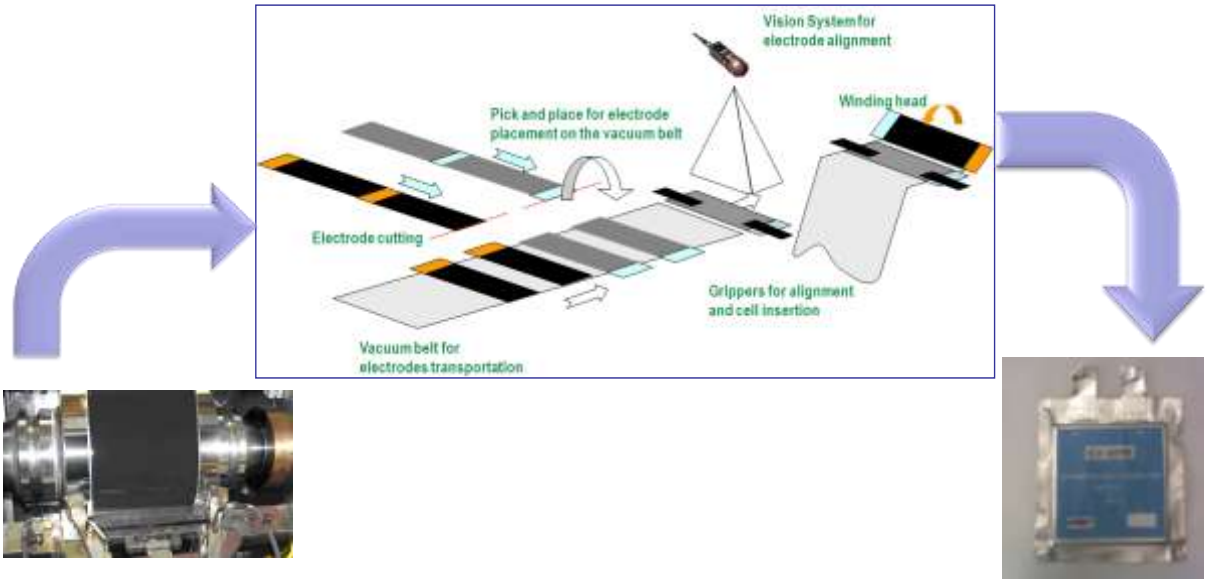

Figure 23. Wound stack pilot process for softpack assembly.

Arcotronics finally assembled the three selected configurations of cells.

Finally, through a defined assembly process, prototype cells have been assembled and put in a dedicated case (see Figure 24).

Figure 24. Prototype symmetric cell.

Prototype cells and modules realization and testing

Three generations of prototype cells have been finally assembled and tested according to a defined test procedure:

1. **Symmetric carbon/carbon cells** with IL-based electrolyte, mainly aimed to analyze the functionality and repeatability of the assembly process. Non-optimized carbon electrodes were used. A set of 6 cells were initially assembled for such purpose. Figure 25 shows the 1st generation of ILHYPOS cells.

Figure 25. Complete set of ILHYPOS symmetric carbon/carbon prototypes with IL-based electrolyte.

2. **Hybrid carbon/ECP cells** with IL-based electrolyte. This was the cell design planned at the beginning of the project. Some prototype cells were finally assembled to verify basic performances and the effect of assembly process on the stability of ECP (see Figure 26).
3. **Asymmetric carbon/carbon cells** with IL-based electrolyte, a novel concept, aimed at meeting project targets by optimizing performances of carbon elec-

trodes and the peculiar features of IL-based electrolyte. Figure 27 shows the final prototype cells.

Figure 26. ILHYPOS hybrid and asymmetric prototypes with IL-based electrolyte.

Table 14 summarizes the overall number of the final prototype produced with their design characteristics.

Table 14. ILHYPOS prototype cells produced with their characteristics.

Cell Type	Voltage, V	Capacitance, F	Number of cell	Number of electrode pairs
Hybrid cell				
CDH6	3.7	300	6	36
Asymmetric cells				
CD6	3.7	424	21	126
CD10	3.7	706	4	40
CD15	3.7	1060	2	30
CD20	3.7	1416	4	80
TOTAL			**31**	**312**

The module design was carried out for different targets, as shown in Table 15:

1. Achievement of 5-10 kW peak power systems;
2. Comparability with commercial products (15-20 V system).

Table 15. Module design analysis with asymmetric cells.

Module code	Cell code	Number of cells	Module Voltage V	Module capacitance F	Total number of modules
MS10_10	C10	10	37.0	35.1	3
MS10_4		4	14.8	88.5	7
MS10_3		3	11.1	118	10
MS15_10	C15	10	37.0	53.1	2
MS15_4		4	14.8	132.75	5
MS15_3		3	11.1	177	6
MS20_10	C20	10	37.0	70.8	1
MS20_4		4	14.8	177	3
MS20_3		3	11.1	236	4

At the end of project, two modules MSD6_5 have been produced (see Table 16).

Table 16. Characteristics of the assembled series-connected modules.

Module code	Cell code	Number of cells	Module Voltage V	Module capacitance F
MSD6_5	CD6	5	18.5	73

The prototype modules have been assembled in order to allow an easy disconnection of the cells, and in order to provide an adjustable pressure to the pack. The pressure seems to be a condition required for the proper functionality of the single cells. Figures 27 and 28 give some details about the module assembly.

Figure 27. ILHYPOS prototype module with 5-cell in series: a) front view; b) side vie.

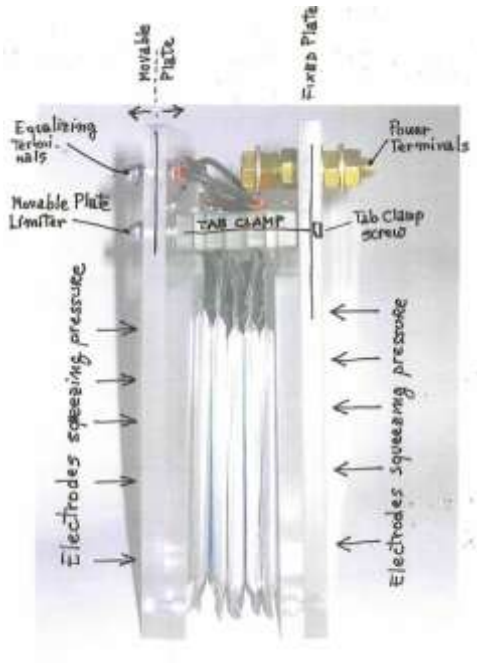

Figure 28. Design details of the ILHYPOS module prototype.

Testing procedure

The ILHYPOS SC test procedure was finalized to the following objectives:

1. Evaluation of performance characteristics of SC.

2. Comparison of SC in a consistent and reliable way.
3. Identification of weaknesses of technology for their development.

The testing work was at the end used, in combination with more electrochemical testing, to characterize prototype cells and to verify their capability to meet project technical targets, mainly in terms of specific power, energy and internal resistance (ESR=Equivalent Series Resistance).

The test sequence for the prototype cells was then aimed at characterizing the basic performances of the cells. Table 17 summarizes the test sequence.

Table 17. Preliminary Test Sequence for mid-term prototype cells.

Test Type	Temperature
Initial Inspection **Weight** **Volume**	Room temperature (RT)
Minimum Parameter Test **Capacitance** **ESR** **Peak and Specific Power** **Specific Energy and Efficiency**	RT, -20 °C, +60 °C

The test procedure included a simple life cycle test (constant current during charge and discharge, depending on the SC capacitance).

The 1st generation of prototype symmetric cells (6 in total) had a maximum capacitance of 450 F (during discharge) in about 90 g of total weight with a maximum specific energy of 31 Wh/kg (based on active materials weight) and more than 1 kW/kg of specific power. The cells lasted more than 22,700 deep cycles before degradation.

Figure 29 shows the prototype cell under test in a climatic chamber.

Figure 29. Symmetric SC prototype in a climatic chamber during test.

The hybrid and asymmetric prototypes have given results close to the designed values only for some of them: for example, a CD6 cell with a designed capacitance of 355 F gave a slightly lower value of 340 F. In general, they showed higher internal resistance of the de-

signed values, demonstrating the needs for further improvements of the scale up and of the assembly process.

3 Dissemination and use

The general rules for using and disseminating the knowledge have been discussed among the participants and incorporated in the approved Consortium Agreement, which complements and somehow recalls most general rules, provided in the *Guide to Intellectual Property Rights for FP6 projects*, (Version 1, 17/03/2004, Research DG) and in the General Conditions, annexed to the ILHYPOS Contract. In addition, suggestions coming from EU publications, such as "A guide to successful communications", have been used to better focus and organize the dissemination activities.

Exploitable knowledge and its Use

Table 18. Key exploitable results and actions.

Exploitable Knowledge (description)	Exploitable product(s) or measure(s)	Sector(s) of application	Timetable for commercial use	Patents or other IPR protection	Owner & Other Partner(s) involved
1. Aqueous process for IL preparation	*Material preparation*	*1. Batteries* *2. Supercapacitors* *3. Fuel cells*	*After 2010*	*A materials patent will be prepared*	***Partic. ENEA (owner)***
2. Bulk preparation of conducting polymers for positive electrodes	*Material preparation*	*1. Batteries* *2. Supercapacitors* *3. Fuel cells*	*After 2010*	*Technology transfer to a company started*	***Partic. CNAM***

- One exploitable result is related to the preparation routes of IL based on an original and cost-effective aqueous process.
- The preparation of electronically conducting polymers (ECP) has been optimized by CNAM and the know-how has been also transferred to a small company for future scale up production.

Other new concepts and ideas have been developed, but the ILHYPOS participants have not identified complete originality aspects, even if the know-how on hybrid, asymmetric and symmetric SC with ILs deserves attention and has been continuously monitored in scientific bibliography, patents and market.

Dissemination of knowledge

The dissemination activities have followed three main channels, mostly related to the characteristics and the mission of the participating organizations in the ILHYPOS project:

1. Scientific papers for international refereed journals for the scientific community have been largely prepared, together with various presentations to national and international conferences. The scope has been to disseminate the results and

have possible feedback from the scientific and industrial target groups to improve and overcome project results, maintaining the activities really challenging at the research and development frontier.

2. The preparation of materials and support to the European Commission to use more official channel, already available, to reach the large audience attending and using the European Union facilities and events, such as: interviews, brochures, posters and other institutional events (Review days, TRA conferences) as well as support to the preparation of periodic EC technical reports.
3. The general public has been mostly addressed in general purpose events, with contribution to questionnaires and interviews and with preparation (not from the project funding) of videos containing information about the project or the technologies studied in the project.

Table 19. Overview table of dissemination activities.

Planned/ Actual Dates	Type	Type of audience	Countries addressed	Size of audience	Partner responsible /involved
7-8/12/2005	HC/FC EC Review Days - Presentation	Research + Industry	**EU + Japan + USA**	100	ENEA
13-15/6/2006	TRA Conference - Poster	Research + Industry	**EU**	≈1000	ENEA
5-6/10/2006	HFP Gen Assembly - Poster	Research + Industry	**EU+Japan+USA**	≈1000	ENEA
30/5/2006	AIM - Presentation	Research + Industry	**Italy**	N.A.	UNIBO
10-15/9/2006	SCI - Presentation	Research + Industry	**Italy**	N.A.	UNIBO
18-23/6/2006	IMLB2006 - Presentation	Research + Industry	**Worldwide**	N.A.	UNIBO
27-31/8/2006	57° ISE - Presentation	Research + Industry	**Worldwide**	N.A.	UNIBO
In press	Journal Power Sources - Paper	Research + Industry	**Worldwide**	N.A.	UNIBO
In press	Journal Power Sources - Paper	Research + Industry	**Worldwide**	N.A.	CIRIMAT
September 2006	EU Publications on H2 + FC Project in FP6	General Public	**Worldwide**		ENEA
December 2007	EVS 23	Research + Industry	**Worldwide**	1500	ENEA
November 2007	COST 542 Workshop	Research + Industry	**Worldwide**	100	ENEA
May 2007	ICAC2007 Presentation	Research + Industry	**Worldwide**	N. A.	ENEA
2006	J. Electrochem. Soc. 153(9), A1685 (2006)	Research + Industry	**Worldwide**	N.A.	ENEA
2007	Journal of Power Sources 165, 922-927 (2007).	Research + Industry	**Worldwide**	N.A.	UNIBO, ENEA, CIRIMAT
2006	ECS Transactions 1, 14	Research + Industry	**Worldwide**	N.A.	UNIBO, ENEA, CIRIMAT
2007	CESEP'07	Research + Industry	**Worldwide**	N.A.	UNIBO
2007	National Meeting	General Public	**Italian**	N.A.	UNIBO
2007	Euro Capacitors 2007	Research + Industry	**Worldwide**	N.A.	UNIBO

2007	*Journal of Power Sources 172*	*Research + Industry*	**Worldwide**	*N.A.*	*UNIBO*
2007	*GEI ERA 2007*	*Research + Industry*	**Italian**	*N.A.*	*UNIBO*
2007	*58th Annual International Meeting of the International Society of Electrochemistry"*	*Research + Industry*	**Worldwide**	*Ca. 1000*	*UNIBO*
2007	*Journal of Power Sources 174 (2007) 89–93*	*Research + Industry*	**Worldwide**	*N.A*	*UNIBO*
2007	*CESEP'07 Presentation*	*Research + Industry*	**Worldwide**	*Ca. 400*	*UNIBO*
2007	*Polymer Batteries Fuel Cells, PBFC2007*	*Research + Industry*	**Worldwide**	*N.A.*	*ENEA*
2007	*Journal of Power Sources 174 (2007)*	*Research + Industry*	**Worldwide**	*N.A.*	*UNIBO*
2007	*Electrochemical Communications 9*	*Research + Industry*	**Worldwide**	*N.A.*	*UNIBO*
2007	*EVS 23*	*Research + Industry*	**Worldwide**	*1500*	*ENEA*
2008	*Journal of Power Sources 178*	*Research + Industry*	**Worldwide**	*N.A.*	*UNIBO*
2008	*Electrochimica Acta 53*	*Research + Industry*	**Worldwide**	*N.A.*	*UNIBO*
2008	*Journal of Power Sources 185*	*Research + Industry*	**Worldwide**	*N.A.*	*UNIBO*
2008	*EUPOC2008 Europolymer Conference*	*Research + Industry*	**Worldwide**	*Ca. 400*	*UNIBO*
2008	*ILED2008 Ionic Liquid for Electrochemical Devices*	*Research + Industry*	**Worldwide**	*Ca. 400*	*UNIBO*
2008	*The 59th Annual Meeting of the International Society of Electrochemistry*	*Research + Industry*	**Worldwide**	*Ca. 1000*	*UNIBO*
2008	*2nd ECC European Chemistry Congress*	*Research + Industry*	**Worldwide**	*N.A.*	*UNIBO*
2009	*Journal of The Electrochemical Society 156*	*Research + Industry*	**Worldwide**	*N.A.*	*UNIBO*
2009	*International Workshop on Distributed Energy Systems: The role of Chemical Sciences and Technologies*	*Research + Industry*	**Worldwide**	*N.A.*	*UNIBO*
2009	*First International Symposium on Enhanced Electrochemical Capacitors – ISEE'Cap09*	*Research + Industry*	**Worldwide**	*Ca. 400*	*UNIBO*
2009	*XXIII Congresso Nazionale della Società Chimica Italiana*	*Research + Industry*	**Italian**	*Ca. 400*	*UNIBO*
2009	*Batteries 2009 Pre-*	*Research + Industry*	**Worldwide**	*Ca. 600*	*UNIBO*

	sentation				
2009	*216th Meeting of The Electrochemical Society*	*Research + Industry*	**Worldwide**	*Ca. 1000*	*UNIBO*
2009	*EVS24 – Best Paper Award*	*Research + Industry*	**Worldwide**	*1500*	*ENEA*
2009	*Contribution for EC Magazine for Green cars*	*General public*	**Worldwide**	*N.A.*	*ENEA*
2009	*Interview for EU Website*	*General public*	**Worldwide**	*1500*	*ENEA*
2009	*Questionnaire SITRO Project*	*Research + Industry*	**European**	*N.A.*	*ENEA*
2009	*H2 Roma Presentation*	*Research + Industry*	**International**	*Ca. 400*	*ENEA*
2009	*ENEA Brochure*	*General public*	**In Italian**	*Ca. 1000*	*ENEA*
2009	*H2 Roma Interview on Website*	*General public*	**In Italian**	*N.A.*	*ENEA*
2009	*ENEA Web Video*	*General public*	**In Italian**	*N.A.*	*ENEA*
From 2005	*Seminar delivered yearly at the "Materials for Energy Storage and Conversion" Eramus Mundus Master Course since 2006 (15 students from world-wide)*	*Higher education*	**European**		*CIRIMAT*

Project Logo

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